

23023

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 1 236 937 A2**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

04.09.2002 Bulletin 2002/36

(51) Int Cl.7: F16J 15/02, C22C 29/00

(21) Application number: 02445014.0

(22) Date of filing: 07.02.2002

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR

Designated Extension States:

AL LT LV MK RO SI

(72) Inventors:

- Ederyd, Stefan  
132 47 Saltsjö-Boo (SE)
- Pauty, Emmanuel  
38130 Echirolles (FR)

(30) Priority: 08.02.2001 SE 0100398

(74) Representative: Taquist, Lennart et al

(71) Applicant: Sandvik AB

81181 Sandviken (SE)

Sandvik AB

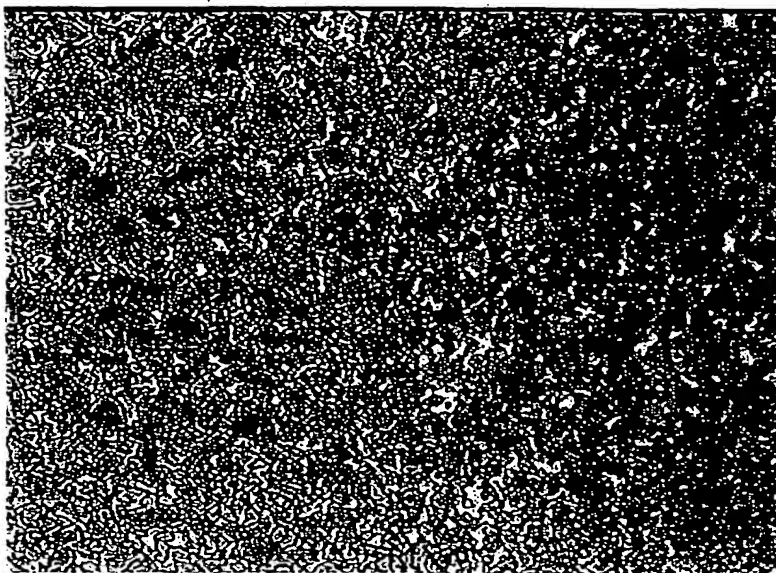
Patent Department

811 81 SANDVIKEN (SE)

(54) **Seal rings for potable water applications**

(57) The present invention relates to cemented carbide seal rings consisting of at least one hard phase in a binder phase based on Co, Ni and Fe giving a content

Fe, Ni and Cr of less than 50 µg/l of each in a leach test with deionized water at 85°C performed according to the requirements of British Standard BS6920: Section 2.6: 1996.



**Fig. 1**

**BEST AVAILABLE COPY**

EP 1 236 937 A2

## Description

[0001] The present invention relates to cemented carbide seal rings for potable water applications satisfying new demands of Fe, Ni and Cr contents.

[0002] Cemented carbide for corrosion resistance demanding applications such as seal rings, bearings, bushings, hot rolls, etc. generally has a binder phase consisting of Co, Ni, Cr and Mo where the Cr and/or Mo addition act as corrosion inhibiting additions. An example of such a cemented carbide is disclosed in US 4,497,660.

[0003] US 6,010,283 and related patents disclose a cemented carbide with Co-Ni-Fe binder phase with 40-90 wt% Co and 4-36 wt% of each of Fe and Ni.

[0004] In cemented carbide seal rings for potable water applications Co and Ni-based binder phase can not be used because of insufficient corrosion resistance. Instead cemented carbide with binder phase based on Ni and Cr have to be used. In the newly approved British standard BS6920 for a cemented carbide to be used in potable water applications a content Fe, Ni and Cr of less than 50 µg/l of each in a leach test with deionized water at 85°C must be fulfilled which is not possible with presently used cemented carbide seal rings.

[0005] It is therefore an object of the present invention to provide seal rings for potable water applications fulfilling the demands of BS6920.

[0006] It has now surprisingly been found that a cemented carbide with a binder phase combining Fe, Ni, Co, Cr and Mo gives such an improvement of the corrosion resistance as stainless steel in hot water. This corrosion resistant property makes it possible to fulfil the demands for the corrosion resistance of British Standard BS6920 for components in contact with potable water. As a result the corrosion resistant cemented carbide can be used in seal rings in potable water applications according to BS6920. Thus, a seal ring with the corrosion properties of stainless steel but with the wear resistance of cemented carbide is obtained.

[0007] Fig 1 shows the microstructure in 1500X magnification of a cemented carbide according to the invention.

[0008] According to the present invention there is now provided cemented carbide seal rings consisting of at least one hard phase in a binder phase based on Co, Ni and Fe fulfilling the requirements of BS 6920.

[0009] Cemented carbide seal rings according to the invention should have a content of binder phase from 5 to 15 wt%, preferably 8 to 11 wt%, most preferably about 9 wt% with the remainder WC with an average grain size of 1.0 µm to 5 µm. The binder phase should be based on Fe, Co and Ni with a composition 35-45 wt% Fe, 15-50 wt% Co and remainder Ni. The Fe/Ni ratio should be 1-1.3. Further the binder phase in addition to dissolved W must contain Cr and possibly Mo. The following relation for the total Cr content shall be satisfied:

$0.05 < \text{wt\%Cr} / (100 - \text{wt\%WC}) < 0.15$ , preferably  $0.055 < \text{wt\%Cr} / (100 - \text{wt\%WC}) < 0.11$ , most preferably about  $0.065 < \text{wt\%Cr} / (100 - \text{wt\%WC}) < 0.085$ .

[0010] The amount of Mo shall be 0.1-3 wt%, preferably <0.5 wt%.

[0011] The total carbon content shall be in the interval of  $6.13 - (0.05 \pm 0.007) \times \text{binder phase (Co+Ni+Fe) content (wt\%)}$ .

[0012] A certain graphite porosity <C02 can be accepted in the interior of the ring, but in the surface region, where corrosion could occur, the graphite can act as a galvanic element and therefore should be avoided. A surface zone thicker than 200 µm free of graphite shall therefore be present.

[0013] The cemented carbide according to the present invention is made by conventional powder metallurgical methods. Powders forming the hard constituents and prealloyed Ni, Fe and Co powders forming the binder phase are wet milled together, dried, pressed to bodies of desired shape and sintered. The powder mixture shall have such a carbon content to give a carbon content of the sintered bodies according to above specified carbon content interval. For the binder phase contents according to the invention a temperature in excess of 1550 °C is suitable. Cooling from sintering temperature shall be made as quickly as possible generally at a speed in excess of 15 °C/min down to 1100 °C.

#### Example 1

[0014] Cemented carbide for seal rings according to prior art were made with the composition of 91 wt% WC, 8 wt% Ni, 0.7 wt% Cr, and 0.3 wt% Mo. Two types of rings with dimension: OD=40 mm, ID=30 mm, height=5 mm (2200 mm<sup>2</sup>) and with dimension: OD=39 mm, ID=31 mm, height=3 mm (1540 mm<sup>2</sup>) respectively, were manufactured for testing.

[0015] The rings were sintered at 1520°C and had a carbon content of 5.64 wt% after sintering and an average WC grain size of 1.5 µm.

[0016] Seal rings according to the invention were made for testing with the same dimensions as above.

[0017] The composition of the cemented carbide according to the invention was:

WC: 91.0 wt%  
FeNiCo alloy: 8.0 wt%  
Mo: 0.3 wt%  
Cr: 0.7 wt%

[0018] The composition of the used FeNiCo-binder alloy was:

Fe:	40.5 wt%
Ni:	remainder
Co	21.1 wt%
Total	C 0.014 wt%
Total	O 0.61 wt%

[0019] The grain size of the WC phase was 1.5  $\mu\text{m}$ .

[0020] The rings were sintered at 1520°C in vacuum for 1 hour.

[0021] The physical properties after sintering were as follow:

Density	14.54 g/cm <sup>3</sup>
Hardness	1200 HV3
Porosity	A00B00C00

[0022] The carbon balance was close to eta-phase formation.

[0023] A good milling and wetting behaviour was observed.

## Example 2

[0024] A corrosion test according to BS6920 was performed with rings used in seal ring applications. The test comprised essentially the following steps:

1. Cleaning of the container with HNO<sub>3</sub> (10 vol%) and deionised water
  2. Cleaning of the sample with tap water (30 min) and rinse three times with deionised water
  3. Immersion of the sample at room temperature during one day in 500 ml of deionised water.
- The rings are placed on PTFE supports (previously washed as in point 1) in order to maintain the rings vertically.

4. Transfer of all but 50 ml of the extract into a sample bottle (cleaned as in point 1).  
Add 5 ml of HNO<sub>3</sub> (70 wt%) to the remaining 50 ml in order to remove any metals adsorbed onto the surface of the container.

Add to the remainder of the extract.

5. Chemical determination of Co, Ni, Cr, Mo and Fe using ICP-spectrometry.
6. Reimmersion of the sample at room temperature in new deionised water six times: five times for one day and once for three days following points 1, 2, 4 and 5.
7. Blank test: following the point 1 to 5 without any sample.

[0025] Test material were rings with two dimensions:  
OD=39 mm, ID=31 mm, height=3 mm (1540 mm<sup>2</sup>)  
OD=40 mm, ID=30 mm, height=5 mm (2200 mm<sup>2</sup>)

[0026] The surface condition was as sintered.

## Materials used in the corrosion test:

[0027] Stainless steel AISI 316 (Fe: Cr18/Ni10/Mo3).

[0028] Plates of steel with about 9000 mm<sup>2</sup> total surface were used instead of rings in the leaching test with water.

## Grade C6N with 0.55 wt%Cr

[0029] Rings with the total area of about 15000 mm<sup>2</sup> were used during the leaching procedure.

[0030] This grade is a common used CC-grade in seal rings for pumps in salt and fresh water.

## Grade C9M (9 wt% of a NiMoCr binder) according to prior art (Example 1)

[0031] Rings with the total area of about 15 000 mm<sup>2</sup> were used during the leaching procedure.

[0032] This grade is used in pumps for corrosive media especially seawater.

Rings according to the invention (Example 1)

[0033] Rings with the total area of about 15 000 mm<sup>2</sup> were used during the leaching procedure.

5 Results:

[0034]

10

15

20

25

30

35

40

45

50

55

# EP 1 236 937 A2

## Results:

Stainless steel AISI 316

Temp. 26°C

Analysis, µg/l	Leaching No	
	1	7
Co	220	<20
Ni	20	<20
Fe	150	<20
Cr	<20	<20
Mo	<20	<20

Temp. 85°C

Analysis, µg/l	Leaching No	
	1	7
Co	60	<20
Ni	2320	<20
Fe	460	<20
Cr	<20	<20
Mo	<20	<20

Grade C6N +0.55 wt%Cr

Temp. 85°C

Analysis, µg/l	Leaching No	
	1	7
Co	480	<25
Ni	6000	210

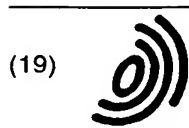
Grade C9M (Prior art, Example 1)

Temp. 85°C

Analysis, µg/l	Leaching No	
	1	7
Co	170	40
Ni	2920	570
Cr	<20	<20
Mo	<20	<20
Fe	370	<20

## Claims

1. Cemented carbide seal ring consisting of at least one hard phase in a binder **characterised** agiving a content Fe, Ni and Cr of less than 50 µg/l of each in a 85°C performed according to British Standard BS6920: Section 2.6: 1996.
2. Cemented carbide seal ring according to claim 1 **characterised in** a content of b: 8 to 11 wt%, most preferably about 9 wt% with the remainder WC with an average a binder phase composition of 35-45 wt% Fe, 15-50 wt% Co and remainder Ni.
3. Cemented carbide seal ring according to claim 2 **characterised in** a Fe/Ni ratio
4. Cemented carbide seal ring according to claim 3 **characterised in** that the binder
5. Cemented carbide seal ring according to claim 4 **characterised in** that the binder of  $0.05 < \text{wt}\% \text{Cr} / (100 - \text{wt}\% \text{WC}) < 0.15$ , preferably  $0.055 < \text{wt}\% \text{Cr} / (100 - \text{wt}\% \text{WC}) < 0.1$
6. Cemented carbide seal ring according to claim 5 **characterised in** that the binder
7. Cemented carbide seal ring according to claim 6 **characterised in** that the binder p of 0.1-3 wt%, preferably <0.5 wt%.
8. Cemented carbide seal ring according to any of the preceding claims **characterised** the interval of  $6.13 - (0.05 \pm 0.007) \times \text{binder phase (Co+Ni+Fe) content (wt\%)}$ .
9. Cemented carbide seal ring according to any of the preceding claims **characterised** in the interior of the ring.
10. Cemented carbide seal ring according to claim 9 **characterised in** containing a surface of graphite porosity.



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 236 937 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:  
15.01.2003 Bulletin 2003/03

(51) Int Cl.7: **F16J 15/02, C22C 29/00**

(43) Date of publication A2:  
04.09.2002 Bulletin 2002/36

(21) Application number: **02445014.0**

(22) Date of filing: **07.02.2002**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**  
Designated Extension States:  
**AL LT LV MK RO SI**

(72) Inventors:  
• **Ederyd, Stefan**  
**132 47 Saltsjö-Boo (SE)**  
• **Pauty, Emmanuel**  
**38130 Echirolles (FR)**

(30) Priority: **08.02.2001 SE 0100398**

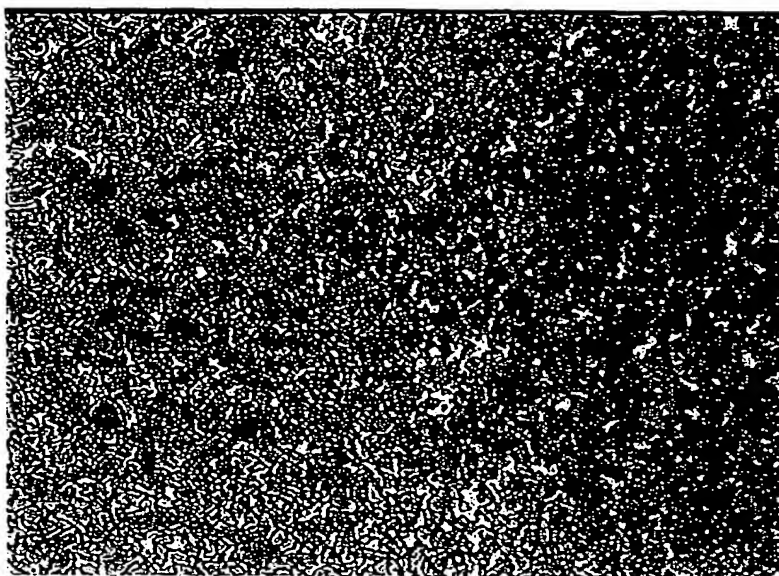
(74) Representative: **Taquist, Lennart et al**  
**Sandvik AB**  
**Patent Department**  
**811 81 SANDVIKEN (SE)**

(71) Applicant: **Sandvik AB**  
**81181 Sandviken (SE)**

(54) **Seal rings for potable water applications**

(57) The present invention relates to cemented carbide seal rings consisting of at least one hard phase in a binder phase based on Co, Ni and Fe giving a content

Fe, Ni and Cr of less than 50 µg/l of each in a leach test with deionized water at 85°C performed according to the requirements of British Standard BS6920: Section 2.6: 1996.



**Fig. 1**

EP 1 236 937 A3

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 44 5014

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-11-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9913119 A	18-03-1999	SE 512668 C2	17-04-2000
		EP 1019557 A1	19-07-2000
		JP 2001515961 T	25-09-2001
		SE 9703202 A	06-03-1999
		WO 9913119 A1	18-03-1999
WO 8002569 A	27-11-1980	SE 420844 B	02-11-1981
		AT 9169 T	15-09-1984
		DE 3069055 D1	04-10-1984
		DK 215280 A ,B,	18-11-1980
		EP 0028620 A1	20-05-1981
		JP 1027143 B	26-05-1989
		JP 56500748 T	04-06-1981
		SE 7904331 A	18-11-1980
		WO 8002569 A1	27-11-1980
		US 4497660 A	05-02-1985
US 6010283 A	04-01-2000	AU 735160 B2	05-07-2001
		AU 8641998 A	16-03-1999
		BR 9814938 A	05-09-2000
		CA 2302308 A1	04-03-1999
		CN 1268192 T	27-09-2000
		DE 1021580 T1	08-02-2001
		EP 1021580 A1	26-07-2000
		ES 2149148 T1	01-11-2000
		WO 9910553 A1	04-03-1999
		JP 2001514084 T	11-09-2001
JP 7286228 A	31-10-1995	NONE	

EPO FORM P/02/98

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☒ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**